

Data Validation SOP

Congener PCB, Rev. 2

Congener PCBs

**Environmental Data Services
Congener PCB (USEPA METHOD 1668A)
Data Validation Checklist**

SITE:

DATE:

SDG:

Y N N/A

Data Completeness and Deliverables

Are the Field Chain of Custody Forms present for all samples?

Is the Narrative or Cover Letter present?

Do the Field Chain of Custody Reports or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical problems, or other comments affecting the quality of the data?

ACTION: Use professional judgment to evaluate the effect of the noted problems on the quality of the data.

Reporting Requirements and Deliverables

Are the following forms present?

Sample Data Summary?

Spiked Sample Summary?

Duplicate Sample Summary?

Method Blank Summary?

Analytical Sequence Summary?

Initial Calibration?

Continuing Calibration?

Y N N/A

GC/MS Displays

Standard and sample SICP's. SICP's must list date and time of analysis; the file name; sample number; and instrument I.D. number?

Percent peak resolution valley?

Integrated area and peak height must be listed for all peaks 2.5 time above background?

All peaks must show retention time at the maximum height?

Laboratory Records

GC/MS Standard and Sample Run Log in chronological order?

Sample Extraction Log?

ACTION: If deliverables are missing call the lab for explanation/ resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the reviewers narrative.

Holding Times

Have any holding times been exceeded for:

aqueous samples 30 days from sample collection to extraction?

soil/sediment samples 30 days from sample collection to extraction?

all samples 40 days from time of extraction to time of analysis?

ACTION: If holding times are exceeded, flag all data as estimated ("J"). Holding time criteria do not apply to PE samples.

If holding times from collection to extraction have been grossly exceeded, use professional judgment to determine whether non-detects shall be rejected.

Y N N/A

Column Performance

Column performance is assessed based on the evaluation of data obtained from the daily (12-hr. shift) diluted combined 209 congener solution.

The retention time for decachlorobiphenyl (PCB 209) must be greater than 55 minutes.

The column must uniquely resolve congeners 34 from 23 and 187 from 182, and congeners 156 and 157 must co elute within 2 seconds at peak maximum.

NOTE: Unique resolution means a valley height of less than 40% of the shorter of the two peaks.

ACTION: If column performance criteria were not met, a detailed discussion of the problems observed and potential effects on analytical data obtained should be included in the data assessment narrative.

Initial 5-Point Calibration

The initial calibration standard solutions (CS1-CS5) must be analyzed prior to any sample analysis. These calibration standards should include all CBs listed at the concentrations specified in Table 5 of Method 1668A. They do not have to be analyzed daily provided the continuing calibration standard met all criteria. The calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze samples.

SIM data were acquired for each of the ions listed in Table 7.

The following criteria must be met:

For IUPAC CBs (3, 4, 15, 19, 28, 37, 52, 77, 81, 138, 156/157, 167, 169, 178, 189, 194, 205, 206 & 208), the two ions for each CB must maximize simultaneously and within 3 seconds of the corresponding labeled isomer ions.

For the other CBs, the 2 ions for each of the CBs being quantified must maximize simultaneously.

The relative ion abundance criteria listed in table 8 must be met.

The relative ion abundance criteria for the labeled internal and recovery standards listed in table 8 must be met.

Y N N/A

For all calibration solutions, the signal to noise ratio (S/N) for all ions of the native compounds must be greater than 10.

For the internal and recovery standards, the signal to noise ratio for all ions must be greater than 10.

The percent relative standard deviation (%RSD) of the five RRFs (CS1-CS5) for the CBs must not be greater than 20 percent.

Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled CBs and internal standards were used. In addition verify that the appropriate internal standard was used for each isomer.

ACTION: If required information were not supplied, notify the lab. If unavailable reject all associated sample data. If any calibration curve standards fail to meet any acceptance criteria, check for re-calibration and re-analysis

Calibration by Isotopic Dilution Procedure

(Native CBs included in the Toxics/LOC CBs list)

To recalculate the response factor for targets quantitated based on isotopic dilution, use the equation:

$$RRF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

Where:

A_n^1 and A_n^2 = integrated areas of the two quantitation ions of isomer of interest (Table 7).

A_{is}^1 and A_{is}^2 = integrated areas of the two quantitation ions of the appropriate labeled compound (Table 7).

Q_n = quantity of the unlabeled CB analyte injected (ng)

Q_{is} = quantity of the appropriate labeled compound injected (ng)

Calibration by Internal Standard

(Native CBs not included in the Toxics/LOC CBs list)

Internal standard calibration is performed at a single point using the diluted combined 209-congener solution (Table 3).

To calculate the response factor for targets based on the internal standard method, use the equation:

$$RF = \frac{(A1_s + A2_s) C_{is}}{(A1_{is} + A2_{is}) C_s}$$

Where:

$A1_s$ and $A2_s$ = The areas of the primary and secondary m/z's for the PCB.

$A1_{is}$ and $A2_{is}$ = The areas of the primary and secondary m/z's for the internal standard.

C_{is} = The concentration of the internal standard (Table 5).

C_s = The concentration of the compound in the calibration standard (Table 5).

Continuing Calibration

At the beginning of each 12-hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all native CBs and labeled compounds. For these tests, analysis of the Cs-3 calibration verification (VER) standard (Section 7.10.1 and Table 5) and the diluted compound 209-congener solution (Section 7.10.2.2 and Table 5) must be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) must be performed until all performance criteria are met. Only after all performance criteria are met, may samples, blanks, IPRs and OPRs be analyzed.

Was the continuing calibration run at the required frequency? _____

ACTION: If the continuing calibration standard was not analyzed at the required frequency, reject all the data.

For native Toxics and LOC CBs, the two SIM ions for each PCB must maximize simultaneously and within 3 seconds of the corresponding ions of the labeled isomers. _____

For the other ions for each of the CBs being quantified, must maximize simultaneously.

Y N N/A

For the continuing calibration standard solution, the signal to noise ratio (S/N) for the CBs ions shall be greater than 10.

The absolute retention times of the labeled Toxics/LOC/window defining standard congeners in the verification test must be within ± 15 seconds of the respective retention times in the calibration. Has this criteria been met?

The relative retention times of native CBs and labeled compounds in the verification test must be within their respective RRT limits in Table 2. Has the criteria been met?

For the internal standards and the recovery standards, the signal to noise ratio (S/N) shall be greater than 10.

The relative ion abundance criteria (Table 8) for all PCB's native shall be met.

Evaluate the concentrations of the Toxics/LOC CBs in the CS-3 VER standard.

For each compound, compare the concentration with the calibration verification limit in Table 6. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. Was this criteria met?

Spot-check continuing calibration concentrations and ion ratios. Verify that the appropriate quantitation ions for the unlabeled PCB's and internal standards were used.

ACTION: If the required continuing calibration fail to meet any of the acceptance criteria, check for recalibration and reanalysis. If not performed reject all data associated with the analyte out of specification in the continuing calibration.

Y N N/A

Sample Data

SIM data were acquired for each of the ions listed in Table 7.

Identification Criteria

- A. For native Toxics and LOC CBs, the two ions for each of the PCB's being quantified must maximize simultaneously and within 3 seconds of the corresponding labeled standard.

For the remaining CBs, the two ions for each of the CBs being quantified must maximize simultaneously.

- B. The integrated ion current for each characteristic ion of the analyte identified as positive must be at least 2.5 times background noise and must have not saturated the detector.

- C. The integrated ion current for the internal and recovery standard characteristic ions must be at least 10 times background noise.

- D. The relative ion abundance criteria (Table 8) for all PCB's found present must be met or ion ratios must be within $\pm 15\%$ of the most recent CS-3 determination.

- E. The relative retention time of the peak for a positively identified CB must be within the RRT QC limits specified in Table 2, or, if an alternate column or column system is employed, within its respective RRT QC limits for the alternate column or column system.

ACTION: Reject (flag R) all positive data for the analytes which do not meet criteria listed in Sections A.

If the criteria listed in section B are not met but all other criteria are met, qualify all positive data of the specific analyte with J.

If the requirements listed in section C are not met but all other requirements are met qualify the positive data of the corresponding analytes with "J".

If the analytes reported positive do not meet ion abundance criteria, section D, or do not meet RRT criteria, Section E, reject (R) all positive data for these analytes. Change the positive values to EMPC (estimated maximum possible concentration).

Y N N/A

Spot check calculations for positive data and verify that the same internal standards used to calculate RRFs were used to calculate concentration.

Compute the concentrations in the extract of the Native Toxics/LOC CBs, using the RRs from the calibration data and following equation:

$$C_{ex} \text{ (ng/mL)} = \frac{(A1_n + A2_n) C_i}{(A1_i + A2_i) RR}$$

Where:

C_{ex} = The concentration of the PCB in the extract, and the Other terms as defined in Section 10.5.1.

Internal Standard Quantitation and Labeled Compound Recovery

Compute the concentrations in the extract of the native compounds other than those in the Native Toxics/LOC standard, in the Labeled cleanup standard, and in the Labeled injection internal standard (except for Labeled CB178), using the response factors determined from the calibration data and the following equation:

$$C_{ex} \text{ (ng/mL)} = \frac{(A1_s + A2_s) C_{is}}{(A1_{is} + A2_{is}) RF}$$

Where:

C_{ex} = The concentration of the labeled compound in The extract. The other terms are defined in Section 10.6.1.

Using the concentration in the extract determined above, compute the percent recovery of the Labeled Toxics/LOC/window-defining CBs and the Labeled cleanup standard CBs using the following equation:

$$\text{Recovery (\%)} = \frac{\text{Concentration found (ug/mL)} \times 100}{\text{Concentration spiked (ug/mL)}}$$

Y N N/A

The concentration of a native CB in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids as follows:

$$\text{Concentration in solid (ng/kg)} = \frac{(C_{ex} \times V_{ex})}{W_s}$$

Where:

C_{ex} = The concentration of the compound in the extract.

V_{ex} = The extract volume in mL.

W_s = The sample weight (dry weight) in kg.

The concentration of a native CB in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted as follows:

$$\text{Concentration in aqueous phase (pg/L)} = \frac{(C_{ex} \times V_{ex})}{V_s}$$

Where:

C_{ex} = The concentration of the compound in the extract.

V_{ex} = The extract volume in mL.

V_s = The sample volume in liters.

Y N N/A

Method Blanks

Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?

ACTION: If the proper number of method blanks were not analyzed, notify the contractor. If they are unavailable, reject all positive sample data. However, the reviewer may also use professional judgment to accept or reject positive sample data if no blank was run.

Were any PCB's found at greater than the method specified minimum level (Table 2) in the associated method blank?

ACTION: All associated samples, which have that PCB reported as detectable at a concentration less than 10 times the blank value, the reported value is changed to non-detectable with an EMPC equal to the reported value of the affected analyte.

Rinsate Blank

One rinsate blank must be collected for each day?

Do any rinsate blanks show the presence of PCB's above the method specified minimum level (Table 2)?

ACTION: If any rinsate blank was found to be contaminated with any of the PCB's, document in narrative notes.

Labeled Compound Recoveries

Were the samples spiked with all the internal standards as specified in the method?

Were internal standard recoveries within the method required limits (25-150%)?

If not, were samples reanalyzed?

ACTION: If the internal standard recovery was outside (25 -150%) flag with "J" all positive data.

Y N N/A

Labeled Injection Internal Standards

There are no contractual criteria for the Internal Standard. However, because it is very critical in determining instrument sensitivity, the Internal Standard area must be checked for every sample.

Internal standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration? _____

Area upper limit = +100% of internal standard area.

Area lower limit = -50% of internal standard area.

Is the retention time of each internal standard within 10 seconds of the associated daily calibrations standard? _____

ACTION: If the internal standard area is outside the upper or lower limits flag all related positive and non-detect data with "J" regardless whether the labeled standard recoveries met specifications or not.

If extremely low area counts (<25%) are reported, flag all associated non-detect data as unusable (R) and the positive data "J."

If the retention time of the internal standard differs by more than 10 seconds from the daily calibration, use professional judgment to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the window defining mix.

Y N N/A

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

For every sample delivery group of 20 or fewer environmental samples there should be one MS/MSD pair analyzed. In order for the MS/MSD to be appropriate for use in qualifying or rejecting associated sample data, the spike level must be within the range of 25% to 400% of the reported sample concentration.

If recovery of the MS is out of the 60 to 140% acceptance range, qualify the value for the analyte in the sample used for the MS/MSD as estimated "J"; use professional judgment in association with signal to noise ratios and internal standard recoveries for the associated sample data to determine the effect on the quality of the associated sample data.

If the precision of the MS/MSD analyses is greater than 50% RPD, then qualify the value for that analyte in the sample used for the MS/MSD as estimated "J"; use professional judgment in association with signal to noise ratios and internal standard recoveries for the associated sample data to determine the effect on the quality of the associated sample data.

Field Duplicate Samples

For every batch of 20 samples or less collected there must be a sample designated as duplicate.

Results of the duplicate samples must agree within 70% relative difference.

ACTION: The duplicate results must be used in conjunction of other QC data. If no hits are reported, precision may be assessed from the internal standard recoveries.

Ongoing Precision and Recovery (OPR)

For every batch of 20 samples or less processed by the laboratory, there must be an OPR processed as well. Has this requirement been met?

Have the calculated percent recoveries for all CBs in the associated OPR met the acceptance limits provided in Table 6?

ACTION: If the laboratory failed to process an OPR sample with the associated field samples, qualify all target analyte results as estimated.

ACTION: If any CB OPR percent recoveries failed to meet the acceptance criteria listed in Table 6, qualify effected sample results as estimated.

As part of the data validation process, the following validation qualifiers and their meanings will be used:

- "U" - Non-Detect - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
- "J" - Estimated Value - The analyte was positively identified; but the associated numerical value is the approximate concentration of the analyte in the sample.
- "NJ" - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
- "UJ" - Estimated Non-Detect - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
- "R" - The sample results are rejected. Due to significant QA/QC problems the analysis is invalid and provides no information as to whether the analyte is present or not. Once the data are flagged with "R", any further review or consideration is unnecessary.

If no determination of the overall bias of a result qualified as estimated can be made, the result will be flagged with "J." If the data reviewer can determine the overall bias for sample data qualified as estimated, the data reviewer will qualify the sample result as either an estimated minimum value (JL) or an estimated maximum value (JH).